Research Article

Synthesis and Spectral Characterization of Praseodymium(III) Complex with New Amino Acid-Based Azo Dye

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Received 24 November 2011; Revised 4 January 2012; Accepted 4 January 2012

Academic Editor: Alvaro J. Pardey

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A new Praseodymium (Pr) (III) complex has been synthesized and characterized by using a new amino acid-based (leucine) azo dye such as N,N-dimethylazoleucine (L1) and 1,10 phenanthroline (L2). Reaction of Pr(III) ion with L1 and L2 in 1 : 2 : 1 ratio in alcoholic medium has been carried out with general formula $[\text{Pr}(\text{L1})_2(\text{L2})(\text{H}_2\text{O})_2]$. Elemental analysis, comparative FT-IR, and ^1H NMR spectral studies of Pr(III) complex with ligands have been shown in this paper.

1. Introduction

Lanthanide complexes attract a growing interest in material science due to their optical and magnetic properties. Special interests are those in which ligands play a role of intramolecular sensitizer for lanthanide luminescence [1]. Therefore, the choice of ligand remains a crucial point, and molecules containing aromatic moieties are very often found to be good sensitizers for lanthanide ions. In the last decade, the new materials based on lanthanide complexes have been studied with particular interest for applications as highly efficient light conversion molecular devices. They can be used in wide range of processes and new technologies, such as fluorescent lighting, electroluminescence color displays, luminescent labels in bioaffinity assays, bioinorganic sensors, and high technology optics and optoelectronic applications [2–8]. Weissman in 1942 reported that lanthanide can be improved by using an intramolecular energy transfer, the antenna effect [1]. Common used ligands are β -diketonates and noncharged adducts like 1,10 phenanthroline or 2,2-bipyridine.

A new azo dye has been synthesized, named, N,N-Dimethylazoleucine, composed of leucine ($\text{NH}_2\text{CH}(\text{CH}_2\text{CH}(\text{C}_2\text{H}_5))\text{COOH}$) as basic moiety and 1,2-dimethylaniline ($\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$) and its Pr(III) complex with 1,10

phenanthroline (heterocyclic compound) (L2) adduct to assess the possibilities of Pr(III) complexes formation and spectral changes that occur due to complexation.

2. Experimental

2.1. Chemicals and Measurements. Elemental analysis was performed with Perkin Elmer 2400 (SAIF Chandigarh, Punjab University). FT-IR spectra were recorded with KBr pellets in 4000 to 400 cm^{-1} on Nicoletet Protege 460 Spectrograph EFT (IIT Delhi). ^1H NMR spectra were recorded with DMSO- d_6 medium on DPX-dix 300 MHz Bruker Avance spectrometer using TMS as an internal reference from 0 to 9 δ ppm (IIT Delhi). Thermogravimetric analysis (TGA) was recorded with F-2nd Perkin Elmer F-second Pyrif Diamond in nitrogen atmosphere (IIT Delhi). Conductivities were measured with digital conductivity meter Model 621E (ranging from 0 to $1999\text{ }\mu\text{S}$, with resolution $1\text{ }\mu\text{S}$).

The lanthanide (Pr, Nd, Ho, and Er) oxides (99.9%) were procured from Acros Organics, India. The 1,10 Phenanthroline monohydrate (99.9%), glycine (99%), sodium nitrite (99%), and N,N-dimethylaniline (99%) were purchased from E. Merck, India. The solvents were of AR or spectroscopic grade, and the chemicals were used as received.

SCHEME 1: Synthesis of N,N-dimethylazoleucine ligand (L1) and Pr(III) complex.

2.2. Preparation of Praseodymium Chloride. Lanthanides(III) chlorides (praseodymium(III) chlorides) ($\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$) with pH from 4 to 6 were obtained from respective Pr(III) oxides by heating with $10 \times 10^{-3} \text{ dm}^3$ AR-hydrochloric acid (HCl) (1 : 1) at 70°C . The resulting solution was rotoevaporated, precipitated, and recrystallized in methanol [9].

2.3. Preparation of Azo Dye (L1) Ligand. Synthesis of azo compound was consisting of two processes: diazotization and coupling (Scheme 1).

2.3.1. Diazotization. 7.1 g of leucine ($\text{NH}_2\text{CH}(\text{CH}_2\text{CH}(\text{C}_2\text{H}_5))\text{COOH}$) was dissolved with 50 mL Millipore water and warmed till a complete dissolution. Now new solution of sodium nitrite (NaNO_2) (2 g) with 10 mL H_2O was added in the above reaction mixture and then allowed to cool in ice bath where temperature was maintained between 0 and 5°C . Cold diluted HCl solution (28 mL) was added dropwise in reaction mixture (in ice bath) with continuous stirring to complete a diazotization process.

TABLE 1: Elemental analysis data of L1 and Pr(III) complex.

Compounds	Found %			Calculated %		
	C	H	N	C	H	N
L1	61.88	7.76	14.59	63.86	8.03	15.96
Pr(L1) ₂ L2H ₂ O	55.94	5.23	12.34	57.44	6.51	13.65

FIGURE 1: FT-IR spectra of L1.

FIGURE 2: FT-IR spectra of Pr(III) complex with L1 and L2.

2.3.2. Coupling. Again a cold solution of N,N-dimethylaniline ($C_6H_5N(CH_3)_2$) (4 mL) in dilute HCl was added to the above-prepared reaction mixture and shook thoroughly for few mins followed by an addition of 20% NaOH (30 mL). Finally the resultant reaction mixture was heated to 60°C with an addition of 8 g NaCl and kept in ice bath (0–5°C) for 3–4 h to obtain precipitate. A dark brown colored precipitate (L1) was filtered and gently washed several times with cold water till it was free completely of all impurities. Then the precipitate was dried at room temperature and then stored in vacuum desiccator filled with P_2O_5 .

2.4. Preparation of 1,10 Phenanthroline (L2) Ligand. L2 ($C_{12}H_8N_2$) is used directly without any further purification.

2.5. Preparation of Pr(III) Complex. The Pr(III) complex was synthesized by reaction of $PrCl_3 \cdot nH_2O$ (1 mol) with L1 (2 mol) and L2 (1 mol) in $L_1:L_2$ molar ratios equal to of 1:2:1. The ethanolic solutions of L1 (20 mL) and L2 (20 mL) were added one by one with continuous stirring to saturated ethanolic solution of $PrCl_3 \cdot nH_2O$. Then the reaction mixture was stirred with an electromagnetic stirrer at 25°C till its volume was reduced to half of its original volume by continuous rotoevaporation. Dark brown colored Pr(III) complex precipitate was obtained and dried at room temperature and kept for 9–10 days. After crystallization

precipitates were washed with distilled water and dried in vacuum desiccator to contents weight.

3. Result and Discussion

The Pr(III) complex is a dark brown colored solid, partially soluble in water, highly soluble in ethanol, DMSO and DMF solvents. The elemental analysis data of the L1 and its Pr(III) complex given in Table 1 is consistent with the calculated results from the empirical formula. The electric conductance measurement in DMF solvent shows the nonelectrolytic nature of Pr(III) complex. The reactions of L1 and L2 with Pr ions are mentioned in Scheme 1.

3.1. FT-IR. The FT-IR spectra of L1 and Pr(III) complex (Figures 1 and 2) ranged 4000–400 cm^{-1} with broad stretching vibrations of all characteristic functional moieties of ligands (L1 and L2), revealing their direct interaction to metal ions (Table 2). On the other hand, spectra of free ligand L1 generally cause sharp signals (Figure 1).

Vibrational spectra of ligand L1 shows a broad vibrational spectrum at 3368.60 cm^{-1} , due to OH-stretching vibration of carboxylic group (Figure 1). Bands at 2970.67 cm^{-1} and 2880.13 cm^{-1} are due to asymmetric and symmetric ν_{C-H} stretching vibrations [10]. A strong and

TABLE 2: Stretching frequencies (cm^{-1}) of functional groups of L1 and Pr(III) complex.

Ligands/complexes	O–H	C=O	N=N	C–N	Aromatic group	C=C	Pr–N
L1	3368.60	1599.56	1597.72	924.44	1508.56, 1435.13, 1351.09, 1314.28	748.08	
Pr	3400.22	1624.09	1620.07	941.71	1518.46, 1436.01, 1349.98	739.16	453.75

TABLE 3: Proton magnetic resonance data (chemical shift δ in ppm) of L1, L2, and Pr(III) complex.

Ligands/complexes	Ha, Hp	Hb	Hc	Hd	Hd, Hs, Ht	He–Hh
L1	2.47	5.34–5.51	5.97–7.19	5.34–5.51	3.06–3.80	
L2						7.63–9.19
Pr	2.59	5.80–5.96	6.42–7.61	3.443	3.12–3.80	9.71

broad absorption bands have been noticed in L1 spectra at 1599.56 cm^{-1} and 1579.72 cm^{-1} , due to overlap of $\nu_{\text{C=O}}$ and $\nu_{\text{N=N}}$ stretching mode of carboxyl group and azo group, respectively. Multiple and dominant peaks from 1508.56 cm^{-1} to 1314.28 cm^{-1} supported the presence of aromatic moiety in L1, and an absorption peak at 748.00 cm^{-1} indicated C–H out of plane-bending vibration of disubstituted benzene ring. A sharp peak at 942.44 cm^{-1} is due to C–N group in L2. Vibrational spectrum of Pr(III) complex is quite different as compared to L2 due to a very strong and broad peak at 3400.22 cm^{-1} , with $\nu_{\text{O–H}}$ stretching vibration of coordinated water (OH) and protonated OH of carboxylic group. As there is very strong interlinked hydrogen bonding, it can be said that the peak assignment for water and that of OH of carboxylic group is due to overlapping of their respective groups (Figure 2). Disappearance of $\nu_{\text{C–H}}$ stretching vibration of methyl group inferred the complex formation. A strong and broad absorption peaks have been noticed in L1 spectra at 1599.56 cm^{-1} and 1579.72 cm^{-1} , which can be due to overlap of $\nu_{\text{C=O}}$ and $\nu_{\text{N=N}}$ stretching mode of carboxyl group and azo group, respectively. Now, shifting of peaks for C=O and N=N stretching vibrations at 1624.09 cm^{-1} and 1620.67 cm^{-1} from its original peak frequencies in L1 spectra found to be characteristic supported the Pr(III) complex formation. Diminishing of bands at 1518.46 cm^{-1} to 1349.98 cm^{-1} of aromatic group supported Pr-ligand coordination bond formation. A characteristic C–H out of plane bending vibration is seen at 850.45 cm^{-1} , indicating the presence of L2 in complex. A peak at 453.75 cm^{-1} indicates the Pr–N [11] coordination bond formation from L1 and L2 to Pr ion, which is constructive support for new coordination complex formation.

3.2. ^1H NMR. The ^1H NMR of L1 or azo compound and Pr(III) complex has been recorded from δ 0 to 10 ppm with $\text{DMSO-}d_6$ to confirm the Pr(III) complex formulation. Present paper will describe all comparative and characteristics peaks signals of ligands and chemicals shifts appeared due to Pr(III) complex formation in Table 3. ^1H NMR spectra of L1 and Pr(III) complex are described in Figures 3 and 4, respectively.

FIGURE 3: ^1H NMR spectra of L1.

^1H NMR spectra of L1 show resonating protons signals in four sets of signals between δ 0–10 ppm. First upfield signal appears as a singlet at δ 2.47 ppm ($J = 0.85\text{ Hz}$) for Ha and Hp protons of four methyl group in ligand L1. The second multiplet resonate in upfield between δ 3.06 and 3.80 ppm ($J = 3.80\text{ Hz}$) assigned to Hd (COOH), Hs (CH_2), and Ht (CH), as it has concluded that Hd, Hs, and Ht protons required approximately same resonating field so a broad multiplet is appeared. Third signal is a downfield doublet with signals between δ 5.34 and 5.51 ppm ($J = 0.89\text{ Hz}$) for Hb of aromatic ring of L1. Forth and last downfield quartet at δ 5.97 ppm ($J = 0.25\text{ Hz}$), 6.09 ($J = 0.25\text{ Hz}$), δ 6.65 ppm ($J = 1.31\text{ Hz}$), and δ 7.19 ppm ($J = 0.33\text{ Hz}$) appeared due to Hc (CH) (Figure 3).

Unlike proton spectra of L1 signals which appeared in four sets, Pr(III) complex has shown similar trends of signals in its spectra but mainly five sets of signals, and all are shifted to downfield indicating Pr(III) complex formation. Downfield shifting of first upfield singlet to δ 2.59 ppm ($J = 0.96\text{ Hz}$) for Ha and Hp protons of four methyl groups of L1. Again a second set of signals like for L1, appeared as multiplet, infers the complex formation by indicating signals

TABLE 4: Thermogravimetric analysis data (Weight loss%) of Pr(III) complex.

Complexes	Temperature (°C)	Weight loss %		Constituents eliminated
		Found %	Calculated %	
Pr(L1) ₂ L2H ₂ O	123.5	0.55%	1.60%	Five water molecules
	296.5	12.44%	15.96%	One L2 molecule

FIGURE 4: ¹H NMR spectra of Pr(III) complex with L1 and L2.

at δ 3.12 ppm ($J = 1.24$ Hz), δ 3.42 ppm ($J = 0.89$ Hz), and δ 3.80 ppm ($J = 1.12$ Hz). These are assigned to three set of protons like Hd (COOH), Hs (CH₂), and Ht (CH). Third signal is a downfield doublet with signals between δ 5.80–5.96 ppm ($J = 1.02$ Hz) for Hb of aromatic ring, and forth and downfield shifted quartet at δ 6.42 ppm ($J = 0.29$ Hz), 6.69 ppm ($J = 0.30$ Hz), δ 7.07 ppm ($J = 1.34$ Hz), and δ 7.61 ppm ($J = 0.56$ Hz) are due to Hc (CH) like L1. Fifth and last downfield broad singlet at δ 9.71 ppm ($J = 1.00$ Hz) assigned to L2 protons (He–Hh) with the coordination of L2 to metal ion (Figure 4).

Due to electron transfer from nitrogen of L1 and L2 to Pr(III) ion, many differences in chemical shifts have been noticed and confirmed an expected coordination of metal ligands.

3.3. TGA. The thermogram of Pr(III) complex [Pr(L1)(L2)-(H₂O)] was examined by TGA in the temperature range ambient to 1000°C carried out in nitrogen atmosphere by heating at 10°C min⁻¹. The thermogram of the Pr(III) complex shows stepwise decomposition and reveals the presence of water molecules in Pr(III) complex (Table 4). Pr(III) complex shows an inflexion point at 123.5°C with a weight loss of 0.55%. Representing the removal of one water molecules coordinated to Pr ion with weight loss compared to calculated 1.60%. The second inflexion point appeared at 296.5°C and represents expulsion of one coordinated

1,10 phenanthroline molecule. The observed weight loss at this temperature is 15.96%, which is found equivalent to calculated weight loss 12.44% for one unit of L2.

4. Conclusion

A new leucine-based azo dye and its complex with Pr(III) were synthesized and characterized successfully. FT-IR spectra supported praseodymium ion coordination with six and two nitrogen atoms of two tridentate L1 and one bidentate L2 ligands, respectively, with specific stretching frequencies at 453.75 cm⁻¹, of nitrogen bonding with metal ion. Prominent singlet between δ 3.12 and 3.80 ppm in ¹H NMR showed a presence of a intact hydroxyl group (OH) of carboxyl (COOH) moiety of the L1 with Pr(III) complex. Thermogravimetric analysis supported the coordination of one water molecules with Pr(III) complex. The molecular structure of metal complex with the ligands has been well established with several techniques described in this paper.

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